ELSEVIER

Catalysis Today 42 (1998) 303–310

CATALYSIS TODAY

# Oxidative and nonoxidative conversion of $C_2$ hydrocarbons on ZSM-5

S.N. Vereshchagin[a,*], N.N. Shishkina[a], A.G. Anshits[b]

[a]*Institute of Chemistry of Natural Organic Materials, Akademgorodok, Krasnoyarsk 660036, Russia*
[b]*Department of Chemistry, Krasnoyarsk State Technical University, Kirenskii Str. 26, Krasnoyarsk 660074, Russia*

**Abstract**

Reaction of $C_1$–$C_2$ hydrocarbon conversion on decationated HNaZSM-5 at 50–400°C under nonoxidative and oxidative conditions is described. Experimental data which show the influence of population density of active surface centres on the course of the reaction are presented. Possible cooperative action of isolated acid centres and participation of radical intermediates in oxidative conversion are discussed.

*Keywords:* ZSM-5; Ethylene; Oxidative conversion

## 1. Introduction

Reactions of hydrocarbon conversion over acidic zeolites are a subject of study which employ IR, NMR, TPD techniques but the mechanism of the reaction is still a subject of discussion [1]. There is only a limited number of studies available which can be used to understand the role and reactivities of intermediates and surface species and that of active sites as a part of reaction mechanism [2]. The complexity of the problem originates from the numerous consecutive and parallel reactions which usually take place over zeolites giving a mixture of different products. Unique character of zeolite framework causes diffusion limitations and produces the so-called "shape selectivity" effect. Moreover catalytic properties of active sites (e.g. acid sites) localized in the zeolite framework can be different from those located in the amorphous material not only because of the different chemical nature but because of a different population density and space arrangement when two 'isolated' active centres can act as a 'binary' one if they are located in the vicinity (e.g. on the opposite sites of the zeolite channel). This effect was proposed to explain the peculiarities of conversion of ethylene oligomers which took place under TPD condition for a number HZSM-5 catalysts with different Si/Al ratio [3].

The objective of the present paper is to give another example of the possible influence of the distribution density of active centres on the reaction of hydrocarbon conversion on zeolites and an attempt to apply this approach to oxidative conversion.

## 2. Experimental

Initial NaZSM-5 type zeolite with composition $(SiO_2)_{45.3}(Na_2Al_2O_4)$ was obtained by direct synthesis. The composition of the starting and decationated materials was determined by the atomic absorption

---

*Corresponding author.

0920-5861/98/$32.00 © 1998 Elsevier Science B.V. All rights reserved.
*PII* S0920-5861(98)00106-0

analysis. An initial zeolite sample of NaZSM-5 was treated with 0.06–0.11 N aqueous solution of $CH_3$-$COONH_4$ for 0.5 h at 50°C to obtain the desired decationation degree. Before an experimental run a sample of zeolite (0.15 g) was treated in dry oxygen flow at 480°C for 2 h and then evacuated in a static vacuum system at $P$=0.1 Pa and 500°C for 0.5 h.

Ethylene adsorption was carried out in the same static vacuum system at $P_{C_2H_4}=8\pm0.3$ kPa and $T$=50°C. The amount of ethylene adsorbed and the rate of adsorption were calculated from the pressure drop, the accuracy of pressure measurements being 1 Pa.

Catalytic experiments are carried out in a conventional fixed bed catalytic set-up equipped with on-line gas chromatograph. Mixtures of gases ($CH_4+N_2O+He$; $C_2H_6+N_2O+He$; $C_2H_4+He$) were prepared prior to use by mixing by individual gases, and mixtures of alcohols+He were prepared using saturator kept at constant temperature. A set of columns is used to analyse products: Carbosieve SII (packed, 2 m), Porapak Q (packed, 2 m), modified $Al_2O_3$ and capillary Squalane (50 m) with He as a carrier gas. Amount of $N_2O$ decomposition sites is determined as an amount of $N_2$ evolved at 340°C after interaction of the sample with repeated pulses of pure $N_2O$ (0.2 sccm).

Temperature programmed desorption of ammonia was employed to estimate acidity of zeolites used. Ammonia was adsorbed on zeolite surface at 200°C, purged with helium followed by standard TPD run (heating rate 10°C/min). A quantity of acid sites was calculated as amount of $NH_3$ desorbed at temperatures above 380°C.

## 3. Results and discussion

### 3.1. *Ethylene conversion at ambient temperature*

The rate of ethylene uptake upon time or $C_2H_4$ coverage for all samples of H-NaZSM-5 zeolites has an unusual shape (Fig. 1). An initial portion of $C_2H_4$ (about $4\times10^{20}$–$5.5\times10^{20}$ molec.$C_2H_4$/g) is adsorbed very quickly and then a decrease of adsorption rate occurs. After a certain period of time (which depends upon the sodium content) an acceleration of reaction is observed. The rate of adsorption reaches a maximum at $6\times10^{20}$–$8.5\times10^{20}$ molec.$C_2H_4$/g and falls down slowly to zero. The maximum of the rate of adsorption is less pronounced in the case of samples with decationation degree greater than 60% because of the partial overlapping with the first fast ethylene uptake and no maximum is found for 100% exchanged sample HZSM-5. Using data in Fig. 1 three different regions of adsorption rate may be resolved: (i) initial fast uptake of ethylene, (ii) acceleration of reaction rate and (iii) decrease of the rate of ethylene consumption.

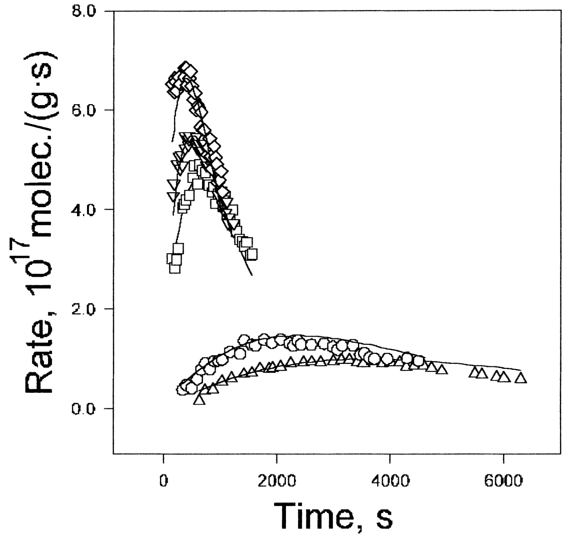

Fig. 1. Variation of adsorption rate of ethylene as a function of time for H-NaZSM-5(45), decationation degree: (△) 13.5%H; (○) 18.7%H; (□) 49.6%H; (▽) 57.4%H; (◇) 67.4%H.

The fast uptake of ethylene appears to be caused by physical adsorption of olefin because it occurs also on sodium form of pentasil (NaZSM-5). For this sample no pressure drop is observed after the first fast adsorption of olefin and $C_2H_4$ is quantitatively removed from the surface under subsequent evacuation or purging with helium at elevated temperatures.

Unlike sodium form of zeolite the heating of the partially exchanged H-NaZSM-5 zeolites which contain adsorbed ethylene does not lead to $C_2H_4$ evolution. Instead of $C_2H_4$ a mixture of saturated and unsaturated hydrocarbons is desorbed that indicates that the reaction of $C_2H_4$ oligomerization has occurred [3]. Therefore the $C_2H_4$ consumption that occurred in stage (ii) and (iii) should be connected with chemical reaction (formation of oligomers).

The slow decrease of reaction rate may be attributed to a few reasons:

- active centres are blocked with molecules of oligomers which cannot be removed from the centres at the temperature of experiments;
- kinetic constant of the reaction of ethylene addition to a surface oligomer species decreases with the growth of oligomer chain;
- growing oligomer chains fill the volume of zeolite framework and prevent ethylene from reacting, the reaction stops when the whole volume is charged.

It should be pointed out that the maximal amount of $C_2H_4$ which can be adsorbed on H-NaZSM-5 does not depend on the sodium content and was found to be about $17\times10^{20}$ molec.$C_2H_4$/g for all samples studied. It is generally accepted that reaction of olefins conversion over hydrogen form of zeolites occurred on acid centres [4]. The number of ethylene molecules converted per acid site (estimated from TPD profile of $NH_3$) at ethylene coverage $17\times10^{20}$ molec.$C_2H_4$/g is equal to the values of 4, 6 and 28 molec.$C_2H_4$ for 100% HZSM-5, 67% and 14% H-NaZSM-5 accordingly. It means that oligomerization degree of ethylene is different for these samples assuming that oligomers do not leave active sites. Therefore it is not the length of the oligomer chain or blockage of active centres which are responsible for the decrease of reaction rate.

The total coverages of $C_2H_4$, $C_3H_6$ and trans-$C_4H_8$-2 which is formed on the surface of 14%H-NaZSM-5 after more than 24 h of adsorption when reaction stops and no additional consumption of olefins occurs are found to be equal to the values of $17.0\times10^{20}$, $11.0\times10^{20}$ and $8.5\times10^{20}$ molec. of hydrocarbons per gram. If we consider the density of oligomers $\rho=0.66$ g/cm$^3$ (0.6595 g/cm$^3$ for $n$-$C_6H_{14}$ at 20°C) then the total volume of formed oligomers can be evaluated to be equal to 0.12 cm$^3$/g for the three olefins used and are close to the void volume of the lattice measured by direct $n$-heptane adsorption at 25°C and $P/P_s=0.4$ which was found to be 0.15 g/cm$^3$. Therefore we can conclude that the progress of the reaction of oligomerization is limited by blockage of the internal volume of the lattice and the drop of the rate of ethylene adsorption is caused by the same reason.

The most interesting feature of the kinetic curves observed is the acceleration of the reaction rate. Let us consider a simple consecutive scheme of ethylene oligomerization (Scheme I) where reaction (1) (or (1a)) is a reaction of formation of an active species Z-$C_2H_4^*$ from ethylene (chain initiation) and reactions (2)–(4) correspond to the growth of oligomeric chains (chains prolongation), the kinetic behaviour of the system described by the scheme depending on relative values of kinetic constants.

Scheme I

$$Z + C_2H_4 \leftarrow K \rightarrow Z - C_2H_4$$

$$\text{Z-}C_2H_4 - k_1' \rightarrow \text{Z-}C_2H_4^* \quad (1a)$$

$$Z + C_2H_4 - k_1 \rightarrow \text{Z-}C_2H_4^* \quad (1)$$

$$\text{Z-}C_2H_4^* + C_2H_4 - k_2 \rightarrow \text{Z-}C_4H_8 \quad (2)$$

$$\text{Z-}C_4H_8 + C_2H_4 - k_3 \rightarrow \text{Z-}C_6H_{12} \quad (3)$$

$$\text{Z-}C_6H_{12} + C_2H_4 - k_4 \rightarrow \text{Z-}C_8H_{16}\ldots \quad (4)$$

It is evident that Scheme I is consistent with the experimental data if the value of kinetic constants $k_1$ and/or $k_2$ are significantly less than that of $k_3$, $k_4$ (as well as any other constants of chain prolongation). Earlier we showed that there was no rate acceleration observed during propene or butene-2 adsorption on the samples studied under the same conditions. It means that there is no slow step in the reaction of $C_3$–$C_4$ olefins with $C_3$–$C_4$ surface hydrocarbon species. Moreover, a preliminary adsorption of $0.3\times10^{20}$ molec.$C_4H_8$/g (which corresponds to $0.6\times10^{20}$ molec.$C_2H_4$/g) on 19% H-NaZSM-5 followed by ethylene adsorption eliminates completely the period of rate acceleration. In this case after the first rapid uptake of $C_2H_4$ (similar to the samples without butene-2 pretreatment) a slow decrease of ethylene consumption occurs, the initial rate of reaction being equal to the value of that observed for 19% H-NaZSM -5 in maximum at $\Theta=0.7\times10^{20}$ molec.$C_2H_4$/g.

Thus we may speculate that the slow step of the reaction includes either activation of ethylene molecules $C_2H_{4(surf)}\rightarrow C_2H_4^*$ (reactions (1) and (1a)) or formation of $C_4$ species (reaction (2)) which are more reactive than the $C_2$ species. Interaction of $C_4$ surface fragments with $C_2H_4$ (reaction (3)) is faster than steps 1 and/or 2.

Fig. 2 shows the dependence of the rate of ethylene consumption measured in maximum at $5\times10^{20}$–$7\times10^{20}$ molec.$C_2H_4$/g upon the number of strong acid centres (high temperature TPD peak of $NH_3$). It is obvious from the plot that a linear correlation exists

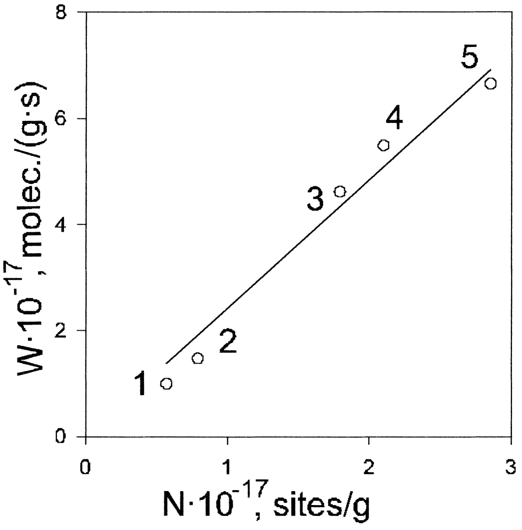

Fig. 2. Variation of maximal adsorption rate $W$ as a function of number of acids sites $N$ for H-NaZSM-5. (1) 13.5% H; (2) 18.7% H; (3) 49.6% H; (4) 57.4% H; (5) 67.4% H.

between the number of strong acid centres and the maximal rate of reaction. According to Scheme I which does not assume the decrease of reaction rate at high coverage the constant rate of ethylene conversion must be observed after some time, the rate of reaction being proportional to the number of active sites $Z$ if kinetic constants of chain prolongation are the same for the different oligomers (i.e. $k_3 = k_4 = \cdots$ etc). If there is some kind of inhibition of reaction at high $C_2H_4$ coverage then the observed linear dependence may also correspond to the equal values of $k_3$, $k_4$ etc. It means that the reactivity of $C_4$, $C_6$, $C_8$ surface species towards $C_2H_4$ attack are identical (or at least almost identical). Moreover, one may consider that the reactions of chain prolongation 3, 4 take place on Bronsted acid sites. The last assumption is based on the well-known fact that sodium removal produces Bronsted acid sites and at low decationation degree one cannot expect any dealumination of stable ZSM-5 framework giving extra-framework species which are also considered to be active in some reaction of hydrocarbon conversion [5]. Lewis acid centres are formed on the zeolite surface at temperatures which are higher than those used in our experiments [6]. Thus it is the isolated structural Bronsted acid centres which are responsible for the reaction of ethylene with $C_4^+$ surface species.

To simulate experimental data a simple kinetic model based on Scheme I is proposed. It is assumed that (i) the limiting step of reaction is the step of $C_2H_4$ activation (reaction (5)); (ii) the kinetic constants of oligomer chain growth do not depend upon the length of the hydrocarbon chain, i.e. reactions of chain prolongation ((3),(4) etc.) may be represented by reactions (6) and (7) and (iii) the rate of reaction is proportional to the void volume of zeolite framework. This scheme does not pretend to be a detailed description but is used as a starting point for further studies.

$$Z + C_2H_4 - k_a \rightarrow ZC_2^* \tag{5}$$

$$ZC_2^* + C_2H_4 - k_p \rightarrow ZR^* \tag{6}$$

$$ZR^* + C_2H_4 - k_p \rightarrow ZR^* \tag{7}$$

The following kinetic equations correspond to the given reactions:

$$\begin{aligned}
&(R_{ZC_2} = k_aP(1-\theta_{ZC_2}-\theta_{ZR}) - k_pP\theta_{ZC_2})\left(1-\frac{\Theta}{\Theta_{\max}}\right)\\
&R_{ZR} = k_pP\theta_{ZC_2}\left(1-\frac{\Theta}{\Theta_{\max}}\right) \qquad (8)\\
&R_{C_2H_4} = xZ_0[(k_aP(1-\Theta_{ZC_2}-\Theta_{ZR})\\
&\qquad + k_pP(\Theta_{ZC_2}+\Theta_{ZR})]\left(1-\frac{\Theta}{\Theta_{\max}}\right),
\end{aligned}$$

where $R_{ZC_2}$, $R_{ZR}$ are the rates of Z-$C_2^*$ and Z-$R^*$ conversions; $R_{C_2H_4}$ the rate of $C_2H_4$ conversion; $q_{ZC_2}$, $q_{ZR}$ are the surface coverage of Z-$C_2^*$ and Z-$R^*$; $\Theta$,$\Theta_{\max}$ the current and total ethylene coverage; $x \times Z_0$ is the number of active sites; and $P$ is the pressure of ethylene.

In these equations $Z_0$ denotes the number of acid sites for totally exchanged zeolite, $x$ is the decationation degree and $(1-\Theta/\Theta_{\max})$ designates the rate decrease at high coverage. The equations are valid if $k_a$ and $k_p$ do not depend on $x$.

Runge–Kutta–Fehlberg integration method was employed for the numerical solution of these differential equations. To fit them to the experimental data, values of $k_a$, $k_p$, $\Theta_{\max}$ were varied for minimizing the error of the fit.

The simulation of individual kinetic curve for a sample using Eq. (8) has shown that the proposed model satisfactorily describes experimental data for all partially decationated zeolites. The values of kinetic constants of chain prolongation $k_p$ are found to be nearly equal for various samples whereas significant difference of $k_a$ are established. Our attempt to describe a whole set of data using Eq. (8) and constant values of $k_a$ and $k_p$ was unsuccessful. From these calculations it is evident that it is possible to describe the behaviour of the system if different values of $k_a$ are used for zeolites with various decationation degrees. Finally a simple power dependence is proposed between $k_a$ and decationation degree $x$,

$$k_a(x) = k_{a0}x^n, \tag{9}$$

where $n$ is a constant and $k_{a0}$ is the kinetic constant for $x=1$.

Using the assumption mentioned above the whole set of experimental data are described, the best values of parameters being $k_{a0}=1.92\times10^{-7}$ $s^{-1}\times Pa^{-1}$, $k_p=5.7\times10^{-7}$ $s^{-1}\times Pa^{-1}$, $\Theta_{max}=8.83\times10^{20}$ molec.$C_2H_4\times g^{-1}$, $n=1.5$. Fig. 1 shows the comparison of experimental points and simulated kinetic curves. The most significant divergences of calculated curves and experimental points are observed at high coverage. It is more likely to be connected to insufficiently exact description of slow down of the reaction rate by the term $(1-\Theta/\Theta_{max})$ and/or distinctions in the reactivity of species possessing various length of hydrocarbon chain. The low value of $\Theta_{max}$ is caused by the fact that initial fast absorption of $4\times10^{20}$–$5.5\times10^{20}$ molec.$C_2H_4\times g^{-1}$ is not taken into account. The sum of this amount and calculated $\Theta_{max}$ is equal to the value of $14.3\times10^{20}$ molec.$C_2H_4\times g^{-1}$ that is close to maximal experimental coverage of $17\times10^{20}$ molec.$C_2H_4\times g^{-1}$.

Constant value of $k_p$ used for all samples implies that the specific activity of zeolites in reaction of chain growth does not depend on decationation degree. From the other hand calculation demonstrates the strong dependence of $k_a$ on decationation degree: Specific activity of the centre in reaction of ethylene activation decreases with decrease of $x$. This is the most unexpected result of the calculation.

No doubt that the activity of zeolite is connected with acid centres. It is known that there is no significant difference in the properties of acid centres at $SiO_2/Al_2O_3=45$ because only isolated structural OH groups associated with $H^+[Si(OAl)(OSi)_3]^-$ fragments are present; the probability of formation of a centre $(H_2{}^+[Si(OAl)_2(OSi)_2]^{2-})$ is negligibly low provided that there is a random distribution of Al in the lattice. This is confirmed by numerous experimental and theoretical studies of ZSM-5. Heat of adsorption of $ND_3$ on high silica zeolites was found to be equal to the value of 140 kJ/mol for all centres of HZSM-5 (Si/Al=30). The same value was found for HM (Si/Al=6.1) at coverage as much as 10–70% indicating that there is no difference in the strength of the isolated acid centres [7]. As only the isolated acid centres are present the decationation procedure appears to have no or slight influence on their properties. If there is no difference in the strength of centres for zeolites with different decationation degree one should expect equal specific activity of the active sites for reaction of ethylene activation and for one of chain growth. Though equal values of $k_p$ were found it is not the case for $k_a$ (reaction of $C_2H_4$ activation). This fact is difficult to explain when homogeneity of acid sites is proposed.

A few possible suggestions may be proposed to explain the results of calculation. First of all one may believe that specific activity of centres is constant but decationation changes the intracrystalline diffusivity of ethylene by blockage of some channels. Although the sodium content in zeolite is relatively low, the location of Na cation in the vicinity of the centre may influence the diffusion rate. This assumption is based on the known fact that in some cases rate of desorption is controlled by diffusion [8]. Another possibility is based on the assumption that in high silica zeolites there are only isolated acid sites $H^+[Si(OAl)(OSi)_3]^-$ but they can act as binary centres if they are located on the opposite sites of the zeolite channel [9]. If this is the case then a correlation should exist between the number of “binary” sites and catalytic activity of the sample. There is no experimental data available concerning the amount of these centres but one may approximately evaluate it assuming random distribution of aluminium in the framework. A probability to find two acid centres closer to each other than a given distance may be calculated using binomial distribution if one knows the total number of positions $N$ which satisfy given requirements and the probability to form acid site on a certain position $\xi$. For partially exchanged zeolite $\xi$ is equal to $x/(M+1)$ ($M=N_{Si}/N_{Al}$, where $x$ is the decationation degree). A value of $N$ may be estimated from structural data for HZSM-5 as an

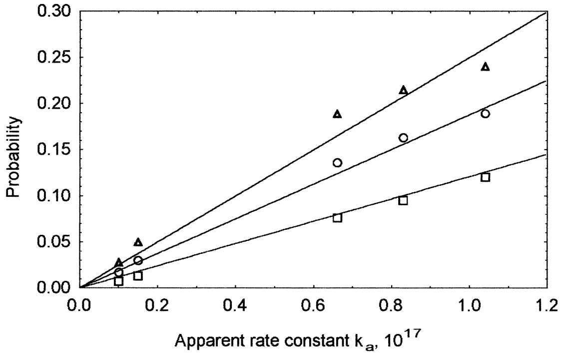

Fig. 3. Correlation between the observed apparent constant $k_a$ and probability to form "binary" acid centre with (△) 48, (○) 36 and (□) 24 space *T*-position.

average number of *T*-atom located within the sphere of a given radius.

Fig. 3 summarizes the results of calculation for 24, 36 and 48 *T*-space position which correspond to the sphere with radius 5.8, 6.7 and 7.7 Å. As a rough estimation all positions are supposed to be equivalent (that is not the case in general). Nevertheless an evident correlation between kinetic constants $k_a$ and probability of "binary" centre formation indicates that there might be joint action which facilitate the activation of olefin. The experimental data presented do not allow to prove this suggestion and a subsequent detailed study is necessary to discriminate diffusion effect from possible conversion on multipoint adsorption/active sites.

### 3.2. *Oxidative conversion of* $C_1$–$C_2$ *hydrocarbons on* HNaZSM-5 *in the presence of* $N_2O$

Unmodified zeolites are not considered to be catalysts for oxidative conversion because of high bonding energy of oxygen and their inability to activate $O_2$ leading to the formation of CO and $CO_2$ at a very low rate. A definite interest in zeolites has appeared after the discovery of the ability of ZSM-5 zeolites to activate $N_2O$ enabling surface oxygen specie to conduct extremely selective conversion of hydrocarbons – ethane to ethylene, benzene to phenol [10,11]. It is found that for both the reactions mentioned catalytic activity does not depend on the acidity of the zeolite and progress of reaction is determined by the active surface oxygen formed from $N_2O$ (by the number of $N_2O$ decomposition sites). It is interesting to study the influence of distribution of these oxidative centres on the progress of the oxidative reactions (10)–(13) over zeolites possessing $10^{16}$–$10^{19}$ sites/g.

The variation of the rate of ethane to ethylene conversion (96–98% selectivity) as a function of a number of $N_2O$ decomposition sites is shown in Fig. 4 (reaction (10)). We found similar linear dependencies for $CH_4$ conversion and for the rate of $N_2O$ decomposition, which corresponds to the published data [11] (reactions (11) and (12)).

$$C_2H_6 + N_2O \rightarrow C_2H_4 + N_2 + H_2O \qquad (10)$$

$$CH_4 + N_2O \rightarrow CO + CO_2 + N_2 + H_2O \qquad (11)$$

$$N_2O \rightarrow N_2 + 1/2\,O_2 \qquad (12)$$

$$C_6H_6 + N_2O \rightarrow C_6H_5OH + N_2 \qquad (13)$$

Therefore the catalytic activity in reactions (10)–(12) does not seem to depend on the density of surface centres because both specific activity and selectivity remain constant for $10^{16}$–$10^{19}$ sites/g. As for reaction (13) studied in detail in [11] a linear dependence of conversion degree on concentration of $N_2O$ decomposition sites was found only for $10^{16}$–$10^{17}$ sites/g, subsequent increase of site concentration to $10^{18}$–$10^{19}$ having no effect on conversion degree. This plateau was attributed by authors [11] to the retarding effect of phenol. It should be pointed out that not only a location but also chemical nature of the centres are still not clear; therefore it is not possible to estimate the density of centres on the surface as it was for acidic centres in the case of $C_2H_4$ adsorption, but to our mind, one should take into account the possibility of interaction of bulky molecules simultaneously with two surface sites when they are present in zeolite in high concentration.

An interesting feature of the oxidative conversion discussed is the distinct product obtained for different hydrocarbons (Table 1). The principal product of ethane conversion is ethylene (i.e. product of dehydrogenation reaction), benzene gives phenol (oxygen insertion into C–H bond) whereas methane is converted to CO and $CO_2$ and traces of aromatic hydrocarbons. An important peculiarity of the reaction of $C_2H_6$ is the formation of a small amount of *n*-butane which can be obtained by the recombination of two ethyl radicals. When methanol, ethanol or ethylene (Table 1) reacted under nonoxidative condition over

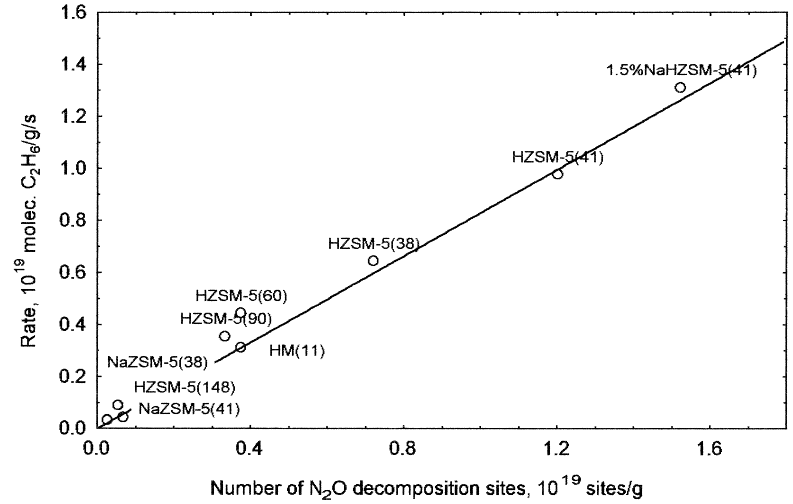

Fig. 4. Variation of the rate of ethane conversion at 390°C (3.6% $N_2O$ 36% $C_2H_6$ in He) as a function of a number $N_2O$-decomposition sites (figures in parentheses denote $SiO_2/Al_2O_3$ ratio).

Table 1
Composition of product formed on NaHZSM(45) at 375°C

| Mixture composition | Conversion (%) | Main products | Concentration of products formed after reaction (vol%) | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | $H_2$ | CO | $CO_2$ | $CH_4$ | $C_2H_4$ | $C_3H_6$ | $n$-$C_4H_{10}$ | $i$-$C_4H_{10}$ | $\Sigma C_4H_8$ |
| $CH_4$:$N_2O$:He<br>1.8:2.2:96 | 30 | CO $CO_2$ | 0.03 | 0.26 | 0.24 | – | – | – | – | – | – |
| $C_2H_6$:$N_2O$:He<br>6.0:5.6:88.4 | 10 | $C_2H_4$ | | 0.02 | 0.03 | 0.03 | 0.34 | 0.023 | 0.00006 | – | 0.003 |
| $C_2H_4$:He<br>4.6:95.4 | ≈0 | – | – | – | – | – | | 0.0014 | – | – | 0.00015 |
| $CH_3OH$:He<br>4:96 | 67 | $CH_3OCH_3$ | – | – | – | – | – | – | – | – | – |
| $C_2H_5OH$:He<br>1.6:98.4 | 91 | $C_2H_4$ | – | – | – | + | 1.5 | 0.0049 | – | – | 0.0015 |
| TPD of ethylene oligomers | | $C_3H_6$ $C_4H_8$ | n/a | | | 0.1 | 3.8 | 24.1 | 0.6 | 5.5 | 41.1 |

zeolites no formation of $n$-butane occurred. Total composition of the products formed from alcohols or ethylene also does not correspond to that found for hydrocarbon+$N_2O$ mixtures. It means that no alcohol or ethylene is the intermediate which is responsible for observed product formation. For us the interaction of surface oxygen with hydrocarbon leads to the formation of intermediates which can give either alcohol (olefin) or CO+$CO_2$ depending on the hydrocarbons and this intermediate appears to possess radical properties.

## Acknowledgements

This work was supported by INTAS and RFBR (project 95-0194).

## References

[1] W.O. Haag, N.Y. Chen, in: L.L. Hegedus (Ed.), Catalyst Design: Progress and Perspectives, Wiley, New York, 1987, p. 181.

[2] J.P. van den Berg, J.P. Wolthuizen, J.H.C. van Hoof, J. Catal. 80 (1983) 139.

[3] A.G. Anshits, S.N. Vereshchagin, N.N. Shishkina, in: Proceedings of the 10th International Congress on Catalysis, Part B Budapest, Hungary, 1992, p. 1661.

[4] J.A. Rabo, G.J. Gajda, Catal. Rev.-Sci. Eng. 31 (1989-1990) 385.

[5] G. Garralon, A. Corma, V. Fornes, Zeolites 9 (1989) 84.

[6] V.L. Zholobenko, L.M. Kustov, V.Yu. Borovkov, V.B. Kazanski, Kinet. Katal. 28 (1987) 965 (in Russian).

[7] E. Paukshtis, IR-spectroscopy in Heterogeneous Acid–base Catalysis, Nauka, Novosibirsk, 1992.

[8] L. Forni, E. Magni, E. Ortoleva, R. Monaci, V. Solinas, J. Catal. 112 (1988) 444.

[9] S.N. Vereshchagin, K.P. Dugaev, N.P. Kirik, N.N. Shishkina, A.G. Anshits, Catal. Today 24 (1995) 349.

[10] S.N. Vereshchagin, L.I. Baikalova, A.G. Anshits, Izv. Akad. Nauk. N8 (1988) 1718 (in Russian).

[11] A.S. Kharitonov, G.A. Sheveleva, G.I. Panov, V.I. Sobolev, Ye.A. Paukshtis, V.N. Romannikov, Appl. Catal. A 98 (1993) 33.